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On: THE MECHANISM OF OXIDE FORMATION IN  
THE INITIAL STAGES OF OXIDATION

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## THE MECHANISM OF OXIDE FORMATION IN THE INITIAL STAGES OF OXIDATION

The major experimental efforts during the past quarter have been directed toward the achievement of a more precise definition of the oxide microcrystallites formed on the tungsten and tantalum substrates in the initial stages of the oxidation reaction. The field emission experiments (see Reports 9 and 10) have revealed the existence of nuclei of a second phase on the surface by virtue of highly localized and sharply defined discontinuities in electron emission intensity. While the nuclei appear more or less simultaneously at regularly spaced intervals on the surface and their number remains approximately constant for specific crystallographic regions of the tungsten substrate, simultaneous nucleation is not observed in the {110} region of tungsten or on any preferred crystallographic region of the tantalum substrate. The non-simultaneous nucleation is apparently characterized by random location of nuclei (i.e., nucleating centers do not occur at regular intervals over the surface) and in many cases by an increasing field enhancement effect with increasing growth. This effect may be attributed to a relatively greater growth rate perpendicular to the substrate than parallel to it (i.e., whisker-like growth).

Of the two types of nucleation, simultaneous nucleation at regularly spaced intervals and essentially lateral growth can be rationalized in terms of the surface diffusion-controlled reaction suggested by others using less well-defined experimental techniques.\* The non-simultaneous nucleation and needle-like growth, on the other hand, require a completely different mechanism. While this type of nucleation can sometimes be attributed to the presence of dislocations on the surface, the probability of many dislocations existing on the field emission substrate is very low due to high temperature annealing and the extremely small surface area.

Two experimental techniques are being developed to define further the oxide nuclei or microcrystallites. Electron diffraction is being used in an attempt to identify the second phase (or phases). Due to the size and shape of the field emitter (ordinarily a five or ten mil wire about 100 mils long), diffraction techniques are difficult. Preliminary trials have been made with blank wires and wires oxidized by heating in air. Standard field emission cathode assemblies have been mounted in a special jig in the diffraction head of a Phillips electron microscope to duplicate anticipated conditions except for the degree of oxide coverage. Diffraction patterns have been obtained from both kinds of wires using a 10-micron aperture and 80-100 KV electrons. Transmission diffraction (i.e., the electron beam being perpendicular to the axis of

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\*For a summary see Gwathmey and Lawless in, H. C. Gatos, ed., "The Surface Chemistry of Metals and Semiconductors," John Wiley and Sons, Inc., 1960, pp. 510-513; or Kubaschewski and Hopkins, "Oxidation of Metals and Alloys," Academic Press, 1962, pp. 53-64.

the wire) has not been successful on either the end of the tip or the cylindrical surface of the shank. Reflection diffraction (i.e., the electron beam being parallel to the axis of the wire) from the cylindrical shank has likewise been unsuccessful. At least two factors have been responsible: a sufficiently large proportion of the beam has not been diffracted, and a relatively flat surface is required because of the small angle of incidence and reflection. These obstacles have been overcome and diffraction patterns obtained by the use of a special jig, holding a wire containing a mechanically produced flat surface parallel to its axis and extending over its entire length. The flat surface has been produced by a standard metallographic polish of the 10-mil wire (while mounted in bakelite) with polishing abrasives of about one-micron in diameter. By using transmission diffraction from evaporated gold foil to determine the camera constant, the product formed on tantalum wires upon heating to about 1000°C in air has been identified as  $Ta_2O_5$ . The next step is to use this technique on a field emitter which has been oxidized to a "known" extent in the field emission microscope under the normal experimental conditions.

Further definition of the shape of the microcrystallites, particularly those which may be protruding extensively above the surface of the substrate, may be obtained by examination of the profile of the emitter after oxidation has taken place in the field emission microscope. Since light microscopy at ~800X has not revealed the presence of the microcrystallites previously observed in the field emission microscope, a specially designed specimen holder will be used to mount the emitter in the conventional electron microscope and thus obtain higher magnification.

In addition, several alterations are being made in the field emission set-up and technique in order to improve the definition of the gas phase. Primarily two techniques have been used in the past for admitting oxygen: resistive heating of an oxygen-saturated silver bead contained in a refrigerated side arm adjacent to the field emission tube, and leaking oxygen into the low-vacuum region of the system. The former technique provides a high oxygen flux at the field emitter without raising the pressure significantly throughout the major portion of the vacuum system - thus permitting a rapid recovery of ultra high vacuum. The limited oxygen capacity of the beads and uncertainty of pressure at the emitter are the primary disadvantages. The outstanding disadvantage of the latter technique is that recovery of ultra high vacuum is difficult. These obstacles can be overcome by the following alterations:

- 1) the side arm containing the silver bead is being replaced by a Granville-Phillips series 9100 variable leak connected to a cylinder of research-grade oxygen, and
- 2) a totally enclosed, manually operated, magnetic valve is being installed in the system so as to isolate the field emission tube and one ionization gauge from the other pumping elements.

The variable leak will provide the desirable high local flux at the tip with virtually unlimited oxygen capacity and good control, and the isolation valve should allow approximately static conditions to be achieved for the purpose of pressure calibration.

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